

Nature of Shear-Induced Primary Nuclei in Isotactic Polypropylene Melt

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Beamline: X27C

Introduction: Although, observations of molecular processes in the formation of primary nuclei prior to actual crystallization are beyond the detection limits of current instrumentation, we have attempted to probe the nature of primary nuclei in sheared isotactic polypropylene (iPP) polymer melt. *In-situ* rheo-SAXS (small-angle X-ray scattering) and -WAXD (wide angle X-ray diffraction) experiments using synchrotron radiation were carried out to evaluate the effects of addition of a high molecular weight atactic polypropylene (aPP) (5 wt %), which is compatible with the iPP matrix but does not crystallize, on the evolution of oriented structures in the sheared iPP melt and its crystallization kinetics. It is unlikely that the aPP chain segments can get incorporated into iPP nuclei or crystal; hence its addition effects, if any, would be seen only in the amorphous melt prior to crystallization.

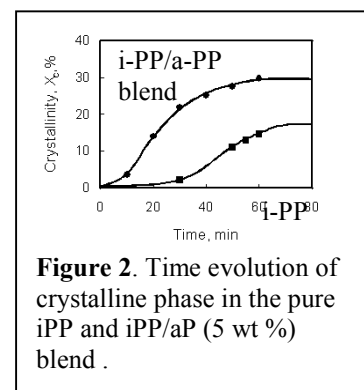
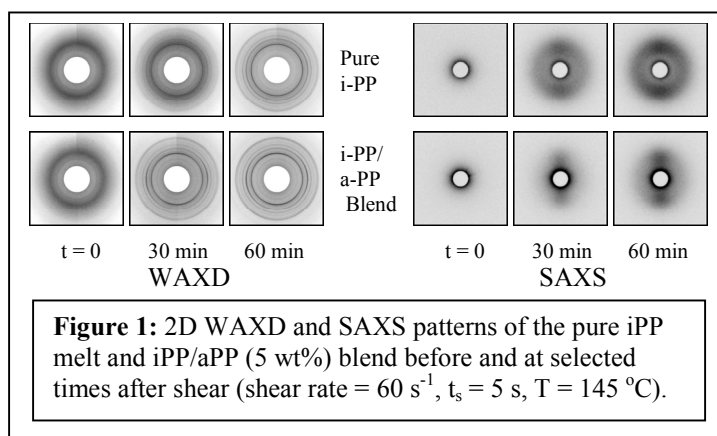
Methods and Materials: Synchrotron X-ray measurements were carried using a Linkam CSS-450 high temperature shearing stage at the X27C Beamline; a 2D MAR CCD detector was used for the detection of 2D scattering patterns. The molecular weights of the iPP resin were: $M_n = 55,000$ g/mol, $M_w = 127,000$ g/mol, $M_z = 230,000$ g/mol and of aPP resin were: $M_n = 256,000$ g/mol, $M_w = 670,000$ g/mol, $M_z = 1,290,000$ g/mol. A solution blending procedure was used to prepare the blend of 95:5 wt% iPP/aPP, which ensures mixing of the two polymer components at the molecular level.

Results: Figure 1 shows two-dimensional (2D) WAXD and SAXS patterns of the pure iPP melt and the i-PP/a-PP (5 wt %) blend at selected times after shear. In the case of blend, the azimuthal breadths in the intensity of crystal reflections are relatively narrow indicating that the crystals orientation is high. On the other hand, crystals orientation is relatively weak in the case of pure iPP. Clearly, iPP crystals orientation is significantly stronger in the blend compared to the pure component. The difference in the extent of orientation (relative intensity of the meridional maxima) between the pure iPP and blend can also be clearly seen in the SAXS patterns. As before, the blend shows a stronger orientation compared to the pure component.

Figure 2 shows that the blend sample crystallizes much faster than the pure iPP polymer sample; $t_{1/2}$ value for the blend is 21 min compared to 45 min for the pure iPP. The increase in the crystallization kinetics can be attributed to the formation of more number of primary nuclei (nucleation) due to stronger orientation in the blend compared to pure iPP.

Discussion: Can the aPP molecule act as a nucleating agent in the conventional sense? We do not believe that a compatible aPP polymer molecule will behave like a typical organic/inorganic nucleating agent that provides a surface for deposition of chain segments (stems) of crystallizing polymer. Could aPP molecule be incorporated into iPP crystal? This is unlikely since each chain segment (or helical stem) in the iPP crystal unit-cell must have a very specific conformation with regard to the pendant CH_3 group. In fact, at first it would seem that aPP molecules should behave as a non-crystallizing, non-nucleating impurity in the iPP matrix without substantially affecting its crystallization behavior.

However, our results clearly showed that it affected both the extent of orientation and crystallization kinetics of iPP. Our explanation is as follows. Although aPP stems cannot be part of the iPP nuclei/crystal, we speculate that the oriented long chains of high molecular weight aPP (that have longer relaxation time and are better aligned) interact with the oriented chain segments of iPP and can aid in maintaining their orientation and alignment for a longer period of time. Thus, within a given period after cessation of shear, less number of oriented stems of iPP relax due to the presence of aPP in the blend compared to pure iPP. And, more number of oriented stems of iPP are available for selection/deposition to form the stable group or bundle (primary nuclei). The result is more number of stable primary nuclei as well as stronger orientation in the blend compared to pure iPP. The interactions of aPP and iPP molecules as well as reorganization of the oriented stems of iPP can only take place in the amorphous melt. We conclude that primary nuclei in iPP most likely consist of liquid-crystalline or mesomorphic bundles of aligned chain segments prior to the formation of crystals.



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